

Translation of International Application as Filed

AUSTENITIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON
ALLOY WITH HIGH CORROSION RESISTANCE TO HOT
CHLORIDE-CONTAINING GASES AND CHLORIDE.

The invention relates to an austenitic nickel-chromium-molybdenum-silicon alloy with additions of silicon.

In plants and aggregates where hot chlorine-containing gases and chlorine-containing deposits occur (chemical plants, thermal waste-disposal facilities, in particular when recycling special waste, plants for the recycling of biomass, large diesel engines, exhaust systems of automobiles) ferritic boiler construction steel is used at temperatures up to 400 C. At higher temperatures, nickel-chromium-molybdenum alloys with 21.5% chromium, 9% molybdenum, 3.7% niobium, 2.5% iron and the remainder nickel and unavoidable impurities (German material number 2.4856) are commonly used (steel code 1995).

However the alloy with the material number 2.4856 is difficult to process. Furthermore, this alloy suffers a considerable ductility loss at temperatures above 500 C, a loss that may result in the formation of cracks in pressure-carrying components and/or those subjected to heavy mechanical stress. To a certain extent, the start of precipitation of the ductility-reducing precipitants can be delayed by lowering the iron content.

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Measures leading to a clear rise in ductility are indicated in the international patent application WO 95/31579 in which a new alloy is described on basis of the alloy according to material number 2.4856 that distinguishes itself through increased hot and cold formability and a greater ductility.

Also the new alloy described in this publication still has some disadvantages. Thus the indicated ductility-raising measures cause the corrosion resistance to gases containing great amounts of chlorine and coatings containing chloride to drop below that of the alloy with the material number 2.4856. Already with this alloy, high corrosion rates occur for reason of constantly rising process and exhaust gas temperatures due to the increase in effectiveness. Alloys of the type 2.4856 are furthermore subject to heat corrosion by sulfate-containing deposits, so that a considerable need for an alloy of a different type, with improved resistance to high-temperature corrosion exists.

It is the object of the present invention to develop an alloy with a resistance to chloric gas corrosion and chloride-containing coatings clearly improved over the state of the art while having at the same time better resistance to sulfate corrosion and a high ductility over the entire temperature range up to 1000 C.

This object is attained by a silicon-containing nickel-chromium-molybdenum alloy which is made up of the following components (in mass %)

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Cr 18 – 22 %

Mo 6 – 10 %

Si 0.6 – 1.7 %

C 0.002 – 0.05 %

Fe 1 – 5 %

Mn 0.05 – 0.5 %

Al 0.1 – 0.5 %

Ti 0.1 – 0.5 %

Mg 0,005 – 0.05 %

Ca 0.001 – 0.01 %

V max. 0.5 %

P max. 0.02 %

S max. 0.01 %

B 0.001 – 0.01 %

Cu max. 0.5 %

Co max. 1 %

Hf and/or Y and/or Zr and/or rare earth : 0.02 – 0.5%, the remainder being nickel and impurities caused by the melting process.

The alloy according to the invention is clearly more resistant to high-temperature corrosion from chloride-containing gases, chlorine-containing ashes, deposits and salt combinations than in the state of the art while being at the same time corrosion-resistant to sulfate corrosion and wet corrosion while remaining highly ductile.

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Advantageous further developments of the object of the invention are found in the sub-claims.

A preferred alloy is characterized by the following alloy components (in mass %):

Cr	18 – 20 %
Mo	8 – 9 %
Si	0.7 – 1.1 %
C	0.02 – 0.015 %
Fe	2.5 – 3.5 %
Mn	0.05 – 0.1 %
Al	0.1 – 0.3 %
Ti	0.1 – 0.4 %
Mg	0,005 – 0.015 %
Ca	0.001 – 0.005 %
V	max. 0.01 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 – 0.001 %
Cu	max. 0.5 %

Hf and/or Y and/or Zr and/rare earth : 0.03 – 0.06%, the remainder being nickel and impurities caused by the melting process.

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The alloy is advantageously suited on the one hand for the production of pipes, in particular composite pipes, sheet-metal, band material, films, wires as well as articles made from these semi-finished products and on the other hand for build-up welding or plating of applied corrosion protection.

The advantageous properties of the alloy according to the invention become apparent from the examples of embodiments indicated below Table 1 shows the example of analyses of charges from the alloy (A-F) according to the invention as well as the comparison alloys (G, H) with components outside the invention. For comparison, the alloy 2.4856 was used. All variants of the alloy were produced from cast blocks by hot rolling followed by cold rolling at room temperature.

The resistance of the alloy according to the invention to chloride corrosion appears from the figs. 1 and 2. For the tests, polished and cleaned test coupons of different test alloys were dipped into an aqueous solution of 1 mol/l NaCl, 0.1 mol/l CaCl₂ and 0.24 mol/l NaHCO₃, were dried at 60 °C and then aged at 750 °C air temperature for 240 hours. This test simulates the stresses such as occur e.g. in exhaust systems of automobile engines (on expansion bellows for the uncoupling of catalytic converter and engine). Fig. 1 shows the metal loss, Fig. 2 shows the corrosion damage determined through metallography at the end of the test. In these investigations it was found that surprisingly the resistance to chloride corrosion could be improved considerably e.g. over the alloy 2.4856 by adding silicon in quantities from 0.6 to 1.7 %.

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The advantageous influence of silicon also becomes apparent in Fig. 3 which shows the corrosion damage of samples determined through metallography, said samples having been placed into a complex medium (chlorine-containing synthetic waste combustion gas ($2.5 \text{ g/m}^3 \text{ HCl}$, $1.3 \text{ g/m}^3 \text{ SO}_2$ / 9 % O_2 , the remainder N_s) with simultaneous subjection to chloride-containing boiler ash) for over 1000 hours at 600 °C. Compared with the charge containing little silicon (e.g. G) the silicon-containing alloy according to the invention suffers distinctly less corrosion attack.

Fig. 4 shows corrosion damage after 1008 hours of cyclical aging of samples which had been coated with a coating consisting of $\text{Na}_2\text{SO}_4/\text{CK1}$ before aging at 750 °C in a chlorine and sulfur dioxide containing. Atmosphere. This test serves to test the resistance to sulfate corrosion. As can be seen in the figure, the alloy according to the invention has clearly lower corrosion rates also with this exposure to corrosion, than the alloy 2.4856 used at this time under such conditions of corrosion.

The outstanding characteristics of the alloy according to the invention can be attributed to the coordination of the alloy elements molybdenum, chrome and iron. The silicon content of the alloy according to the invention should be from 0.6 % to 1.7 %, since the corrosion-resistant effect of the silicon no longer occurs with lower silicon contents, and since greater contents of silicon result in the appearance of embrittling silicides and a distinct loss of ductility, in particular at temperatures in the middle range (500 – 800 °C).

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With silicon content from 0.5 to 1.7% the notched bar impact value , measured on ISO V notched bar samples, does not drop below 100 J/cm even after 1000 hours aging at 600 °C, as shown in Fig. 5.

The molybdenum content of the alloy according to the invention is limited to 10 % since, as shown in Fig. 4, the risk of sulfate corrosion increases with higher molybdenum contents. Molybdenum content is necessary in order to avoid wet corrosion in case of falling short of the dew point.

The chrome content of the alloy according to the invention should be between 18 and 22% in order to ensure sufficient corrosion resistance. Higher chrome contents render the workability of the nickel-chrome-molybdenum alloys distinctly more difficult.

In addition, the alloy should contain hafnium and/or rare earth and/or zirconium and/or yttrium if improved adhesion of protective oxide layers is required for specific applications, e.g. in the automobile exhaust systems at high temperatures and/or in case of rapid temperature changes. The total of these reactive elements should however not exceed 0.5 %.

The iron contents of the alloy according to the invention is limited to a maximum of 5% since higher iron contents in chloride-containing media involve the danger of easily volatile iron chlorides being formed. A minimum content of 1 % is however required in order to ensure the workability of the alloy.

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The carbon content of the alloy according to the invention is limited to a maximum of 0.05, as higher carbon contents involve the risk of intercrystalline corrosion.

The titanium and aluminum contents are limited respectively to a maximum of 0.5 %; the actually undesirable content in niobium is limited to 0.5 % because these elements may result in a loss of ductility at medium temperatures due to the formation of intermetallic phases. The total of niobium, aluminum and titanium additives should not exceed 1 %. A minimum content in oxygen-affinitive elements aluminum, titanium, magnesium and calcium is however necessary in order to ensure good resistance to oxidation. The manganese content should be at least 0.05 % for processing reasons, but should not exceed 0.5% because higher contents in manganese have an unfavorable effect on the resistance to oxidation. To improve workability, 0.001 – 0.01 % in boron are also alloyed into the mix. The phosphor and sulfur contents should be kept as low as possible because these surface-active elements reduce the corrosion resistance at high temperatures as well as the ductility of the alloy.

The alloy according to the invention can be used for bands, films, sheet metal, pipes (seamless or welded), wires, for applied welding, applied plating or as composite pipe.

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The alloy according to the invention can be produced by ingot casting as well as by continuous casting following melting in a vacuum induction furnace or open melting. Recasting of the alloy is possible but not absolutely necessary. Hot-forming is achieved by forging, hot rolling or continuous pressing, and cold forming by cold rolling, wire pulling or by means of a pilger mill. The production of composite materials, e.g. plating on carbon steel, can be effected by means of one of the customary application welding processes, by cold or hot rolling of sheet metal or bands, by explosive cladding or by one of the customary process in the production of bi-metal pipes.

Due to its excellent resistance to chlorination, the alloy is especially well suited as band and sheet metal, pipe or plating material for utilization in hot chlorine-containing gases or in presence of chloride containing coatings, such as occur in chemical plants, in thermal treatment plants for chlorine-containing chemical waste and contaminated floors as well as in automobile exhaust systems (expansion bellows for the uncoupling of catalytic converter and engine). The excellent resistance of the alloy to complex, corrosive saline deposits (furnace ash) renders the alloy also suitable for utilization as plating and construction material in thermal waste disposal plants, in large diesel motors, in plants for the obtention of energy from biomass and in plants of the cellulose industry.